1st midterm F '91 Name key
Chem 130A

1. One mole of an ideal gas ($C_V = {}^3/_2R$) at 20°C and 1 atm pressure is: A) isothermally, reversibly expanded to twice the initial volume.

Calculate q, w, ΔE and ΔH for this process.

$PV = nRT$

$P = \frac{nRT}{V}$

isothermal so $\Delta E = 0$ $\quad q = -w$

reversible $\quad w = -\int P dV = -\int \frac{nRT}{V} dV = -nRT \ln\left(\frac{V_2}{V_1}\right)$

$= -8.31 \cdot 293 \cdot \ln 2 = -1.69 \text{ kJ}$

so $q = 1.69 \text{ kJ}$

$\Delta H = \Delta E + \Delta(PV) = 0$

From point A) the temperature of the gas is raised to 80°C, keeping the volume constant.

$20^\circ C \to 80^\circ C \quad \Delta T = 60^\circ$

Calculate q, w, ΔE and ΔH for this process.

Const vol $\quad w = 0 \quad \Delta E = q = \int_{20}^{60} C_V dT = \frac{3}{2}R \cdot 60 = 0.75 \text{ kJ}$

$\Delta H = \Delta E + \Delta PV = \Delta E + \Delta(nRT) = \Delta E + R\Delta T = \frac{1}{2}R \cdot 60$

$= 0.25 \text{ kJ}$

In a separate experiment the same gas is first heated to 80°C, then is isothermally expanded to twice its original volume.

Calculate ΔE and ΔH for this process.

Since ΔE & ΔH are state functions the path doesn't matter

so $\Delta E = 0.75 \text{ kJ}$

$\Delta H = 0.25 \text{ kJ}$

2. A mountaineer caught in a rainstorm might easily absorb 1 liter of water in her clothing. If it is windy, and this amount of water is evaporated at 20°C, how much heat would be absorbed from the body in the process?

Heat of vaporization = 2447 $\frac{kJ}{kg}$ @ 20°C Table 2.2

Since 1 l = 1 kg 2447 kJ would be absorbed

How many grams of sugar (table sugar = sucrose) would the body have to burn {aerobically metabolize: $C_{12}H_{22}O_{11} + O_2 \rightarrow CO_2(g) + H_2O(liq)$} to replace that heat?

MW

2·12 = 144

22·1 = 22

11·16 = 176

342 g/mol

Sucrose $\Delta H_f^0 = -2222.1 \frac{kJ}{mol}$

CO_2 $\Delta H_f^0 = -393.5 \frac{kJ}{mol}$

H_2O $\Delta H_f^0 = -285.8 \frac{kJ}{mol}$

balance rxn $C_{12}H_{22}O_{11} + 12\,O_2 \longrightarrow 12\,CO_2 + 11\,H_2O$

$$\Delta H_{comb} = 12\cdot(-393.5) - 11(285.8) + 2222.1 = -5644 \frac{kJ}{mol}$$

2447/5644 = 0.43 mol ⟶ 147 grams

If we assume that the mountaineer weighs 60 kg (all of which we may assume behaves like water), what drop in body temperature would occur if no heat were generated?

$$C_p(H_2O) = 4.18\ J/g/K \cdot 60{,}000\ g = 250\ kJ/K$$

$$\frac{2447\ kJ}{250\ kJ/K} \sim 10°K\ \text{drop!}$$

$f \rightarrow u$

3. A biochemistry student noticed the protein she was interested in being degraded. She thought it might be happening through proteolysis of unfolded protein. After searching in recent journals she found a calorimetric study of this protein which gave T_m = 55°C, $\Delta H_{unfolding}$ = 400 kJ/mol, and ΔC_p = 4.5 kJ/mol/K. (remember $\Delta C_p = (C_p^u - C_p^f)$, and T_m is the midpoint temperature for the unfolding transition, at which [folded]=[unfolded]) For a solution with a total protein concentration of 100 µM, what would the concentration of unfolded protein be at 25°C?

$\Delta G = \Delta H - T\Delta S$ $\qquad$ $\Delta H(25°C) = \Delta H(55°) + \Delta C_p \Delta T$

$\Delta G(55°C) = 0$ $\qquad$ $\Delta S(25°C) = \Delta S(55°) + \Delta C_p \ln(T_2/T_1)$

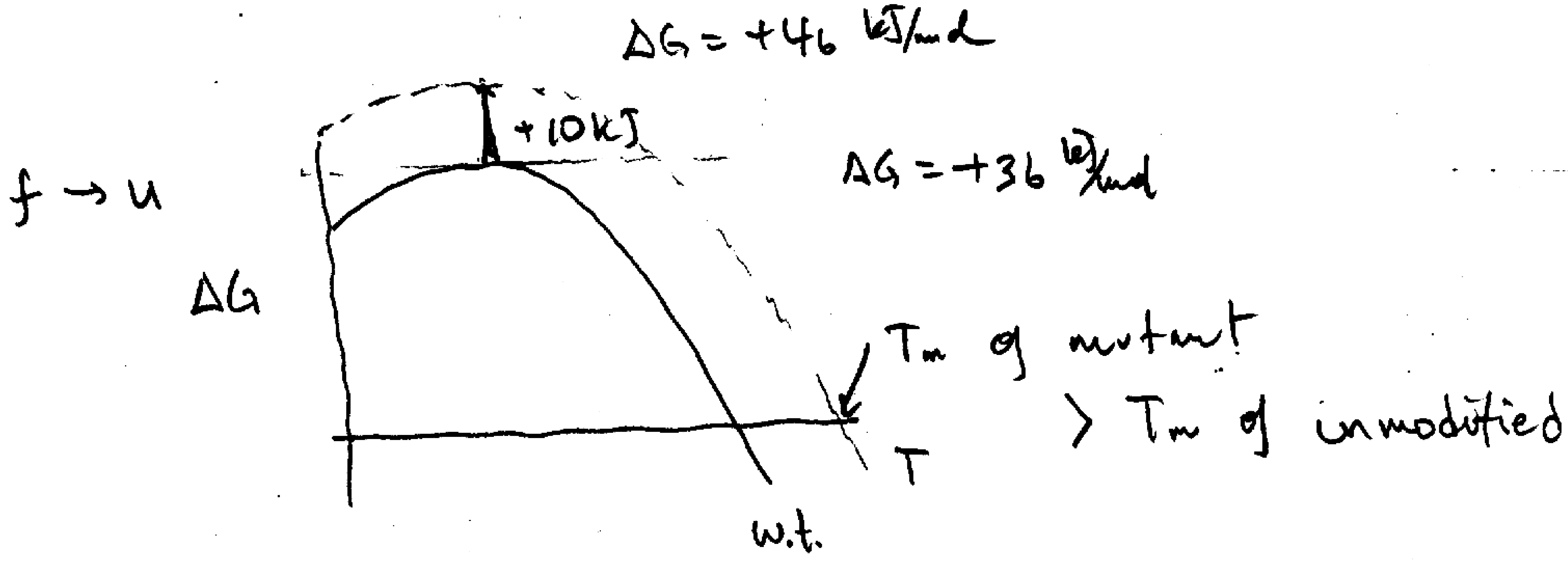
so $\Delta S(55°) = \frac{\Delta H(55°)}{328\,K} = \frac{400\,kJ/mol}{328\,K} = 1.22\,\frac{kJ}{mol\,K}$

$\Delta G(25°) = \Delta H(55°) - 298\,\Delta S(55°) + \Delta C_p\left((298-328) - 298\ln\left(\frac{298}{328}\right)\right)$

$= 36.58\,kJ/mol + 4.5\,(-1.416) = 30.2\,kJ/mol$

$K = e^{-\Delta G/RT} = 5\times10^{-6} = \frac{[u]}{[f]}$ $\quad$ $[f] \approx 100\,\mu M$ $\quad$ $[u] \approx 5\times10^{-10}\,mol/L$

As part of her research project this student changed an amino acid in the known structure of this protein to make a new "salt bridge" (ionic + ↔ - charge interaction). Based on other proteins she thought this should lower the free energy of the folded structure, but not the unfolded form, giving an increase in ΔG of unfolding of +10 kJ/mol. If this ΔΔG is assumed to be temperature independent, would the T_m increase or decrease? Justify your answer by drawing appropriate protein stability curves {ΔG(f→u) vs. T}, labelling them appropriately.



5. A student had laboriously chemically synthesized an RNA oligomer: AAAAAAAUUUUUUU, two molecules of which can for a double helix in solution: $2\ r(A_7U_7) \rightleftharpoons r(A_7U_7)_2$
He was afraid to heat it too high since it might be hydrolyzed, but could determine that in a solution with a **total** concentration of $r(A_7U_7)$ of 100 µM at 37°C the duplex is 10% dissociated. From a table of stacking energies determined for other nucleic acids he could calculate that ΔH° for duplex formation in his sequence should be −450 kJ/mol. From these data determine what the T_m for the duplex should be in this sample.

for nucleic acids $\Delta C_p \sim 0$ ...

$$\Delta G(T) = \Delta H(37°) - T\ \Delta S(37°)$$

if total conc is 100µM then at 37°

$45\,\mu M = [duplex]$ and $10\,\mu M = [dissoc]$

for rxn as written $K_{eq} = \frac{[duplex]}{[dissoc]^2} = \frac{45\,\mu M}{(10\,\mu M)^2} = 4.5 \times 10^5$

at 310K $\Delta G = -RT \ln K_{eq} = -33.5\,kJ/mol$

to get $\Delta S(37)$ use $\Delta G = \Delta H - T\Delta S$

$$\Delta S = \frac{-\Delta G + \Delta H}{T} = \frac{(-33.5 + 450)\,kJ/mol}{310} = -1.344\ \frac{kJ}{mol}$$

to get T_m we want $[duplex] = 25\,\mu M$, $[dissoc] = 50\,\mu M$ — equal number of strands in each

$K = \frac{25\,\mu M}{(50\,\mu M)^2} = 10^4$ so $\Delta G = -RT_m \ln K = -76.57\ T_m\ \frac{J}{mol}$

$(-0.0766) \cdot T_m = -450 - T_m(-1.344)$ $T_m \stackrel{\wedge}{=} 317\,K$